

*Full Length Research Paper*

# Enhanced superconducting properties of the Pb doped trilayer high-temperature ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$ ) cuprate superconductor

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A ceramic superconductor compounds with the composition  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$  were prepared by solid state reaction from the principle routs like Bi-2212,  $\text{Ca}_2\text{CO}_3$  and CuO with high purity of 99.99%. Different measurement such as resistivity measurement, X-ray diffraction (XRD) and scanning electron microscope (SEM) were made to show the improvement in the superconductivity of the high phase. The lattice constants are obtained for undoped and Pb doped samples with different values of n. The critical temperatures ( $T_c$ ) of the high temperature superconducting cuprate (HTSC)  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$  were obtained to be  $T_c = 108\text{K}$  for the undoped sample and equal to 133, 115, 147 and 127K for  $n=3$ ,  $n=3.5$ ,  $n=4$  and  $n=4.5$  Pb doped systems, respectively.

**Key words:**  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$ , HTSC, Pb doping, Electrical Resistivity, XRD, SEM.

## INTRODUCTION

Since the discovery of the Bi-Sr-Ca-Cu-O superconducting compounds (Maeda et al., 1988), a great deal of work has been done to prepare the high-critical temperatures ( $T_c$ ) phase. The most common method used to synthesize these superconducting oxides is the solid state reaction method (Maeda et al., 1988; Koyoma et al., 1988) which consists of the mixing nominal compositions of high purity compounds such as  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$  and CuO, pelletization of calcined powder, under a pressure of 4 to 6 tons/cm<sup>2</sup> and heating the mixed powders for 10 to 20 h at 800 to 820°C. The formation of single high- $T_c$  Bi-2223 phase however, is very difficult due to the appearance of other superconducting phases such as Bi-2212 or non superconducting phases. The most effective methods to enhance the volume fraction of the high- $T_c$  phase were found to be:

1) By starting from composition with surplus Ca and Cu

than the possible ideal composition of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  (Koyoma et al., 1988); by prolonging the sintering (Nobumasa et al., 1988) which is necessary to from extra layers of Cu-O<sub>2</sub> and Ca planes into the layer structure of the low - $T_c$  phase.

2) The annealing in an atmosphere with low oxygen pressure (Nobumasa et al., 1988; Mizuno et al., 1988) which is effective in lowering the reaction temperature and enhancing the stability of the high -  $T_c$ .

3) The substitution of Pb for Bi (Takano et al., 1988; Usai et al., 1988) or the addition of Pb in the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  (Uehara et al., 1988) is very effective in increasing the high- $T_c$  phase. It was found that Pb has a catalytic effect on the reaction to from the high- $T_c$  phase, and a certain amount (about 0.3 mole) of Pb to the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  compound is necessary for the occurrence of this reaction (Usai et al., 1988). Furthermore, the Pb has a role in the stabilization of the high- $T_c$  phase (Takano et al., 1988).

Uehara et al. (1988) studied the magnetic measurement of  $\text{BiSrCaCu}_2\text{O}_x$  and they estimated the high- $T_c$  volume fraction to be 21%. Kumakura et al. (1988) investigated the upper critical field of  $\text{BiSrCaCu}_2\text{O}_x$ ,

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with Tc above 100K. They found that at zero fields, the majority of transition occurred above 103K a zero resistivity was attained below 80K, but as the magnetic field increased, the low temperature portion of transition curve shifts to low temperature, resulting in abroad transition. Matsuoka et al. (1990) investigated the effect on the superconducting behavior of Bi-Sr-Ca-Cu-Pb-O system, and found no effect on the Tc, but is effective in increasing the volume fraction of the Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> compound.

Wu et al. (1992) investigated the effect of sintering temperature and duration on the formation of the 110K phase, in samples of nominal compositions of (Bi<sub>3.2</sub>Pb<sub>0.3</sub>)Sr<sub>4</sub>Ca<sub>x</sub>Cu<sub>y</sub>O<sub>z</sub>. They observed that the optimum compositional rang for obtaining large fraction of high -Tc phase (Tc=105K) occurs between PbBi-4457 and PbBi-4468.

The Bi:2223 phase has attracted considerable interest due to its higher Tc and the potential for applications. One of the reasons for the low critical current densities J is the granular nature of this sintered high temperature superconducting (HTS) compound. It is difficult to prepare single phase material for Bi:2223 phase. The Bi:2212 was frequently observed as a major impurity phase in Bi:2223 samples because of its greater thermodynamic stability with respect to the Bi:2223 phase. The partial substitution of Pb in Bi sites enhances chemical stability and promotes the formation of the 2223 phase (Pop et al., 2006).

Kovaleva et al. (2004) presented systematic study of the c-axis lattice dynamics in Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>4+2n</sub> (n=1, 2, 3) cuprate superconductors (Bi2201, Bi2212 and Bi 2223) based on spectral ellipsometry investigation on single crystal and comparing them with theoretical shell model calculation.

The observation of the multilayer band splitting in the optimally doped trilayer cuprate Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10+δ</sub> (Bi2223) by angle-resolved photoemission spectroscopy is reported by Ideta et al (2010). They obtained values of energy gaps 43 (m eV) and 60 (m eV) larger than those for the same doping level of the double-layer cuprates, which leads to the large value of Tc in Bi2223. The aim of this work is to study the enhancement of the superconducting properties of the Pb doped trilayer high-temperature (Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4δ</sub>) cuprate superconductor.

## EXPERIMENTAL

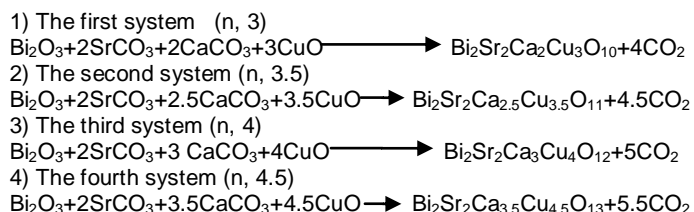
### Materials

The samples were prepared by the solid state reaction method using highly pure 99.99% powders of Bi<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub> and CaCO<sub>3</sub>, CuO, with appropriate weights in proportion to their molecular weights through the following chemical reaction. Four type of superconductors systems were obtained, namely, Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4δ</sub>, Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub>+Pb, Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2.5</sub>Cu<sub>3.5</sub>O<sub>11</sub>+Pb, Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>3</sub>Cu<sub>4</sub>O<sub>12</sub>+Pb and Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>3.5</sub>Cu<sub>4.5</sub>O<sub>13</sub>+Pb. The preparation

of ceramic superconductor by solid state reaction includes a series of stages as shown in the following, measuring the weight of each reactants with the required amount, using sensitive balance with (4-digits), type (STATON)462AL.

### The chemical reactions

The systems were prepared by mixing appropriate amount of the sating materials through the following chemical reactions:



### Sample preparation

The mixture for each specimen was prepared by homogeneously mixing and grinding prescribed amounts of powders into a gate mortar. Appropriate amounts of these powders were mixed with alumna mortar and pestle for 2 h in 2- propanole and dried. The calcinations process performed at 810°C for 16 h by heating rate of 60°C/h, then cooled to room temperature with a rate of 60°C/h in order to remove the CO<sub>2</sub> from the mixture as gas and then crushed into fine powder. The calcinations and grinding procedure were repeated at least three times. This ensure the completely evolvment of CO<sub>2</sub> from the mixture. The resulting powder was pressed into pellets by using cylindrical die set with a stainless steel cylinder of 13 mm diameter and 1.5 to 1.8 mm thickness using manually hydraulic press PERKIN-ELMER, under a pressure of 0.5 GPa. The mixture with the final step of sample preparation was treated with high temperature and causes particles of the materials to join together, and gradually reduce the volume of pore space between them. The powder is compacted into a pellet shape with a certain pressure and then the powder particles was in contact with one another at numerous sites, with significant amount of pore spaces between them.

In order to reduce the boundary energy, atoms diffuse to the boundaries, permitting the particles to be bound together and eventually causing the pores to shrink. If sintering is carried out for a long time the pores may be eliminated and the material becomes dense. The programming data for this process include the rate of heating 60°C/h up to 860°C for 130 h with the flow of oxygen gas of about 1.25 L/min and then with slow rate of cooling 30°C/h down to room temperature. Resintering the pellets was done for 90 to 130 h using the same method as described earlier.

### Doping process

The addition of Pb was done after the calcinations. At the end, the weight of the powder was measured. Then 6% wt of PbO was added as a doping. The mixture of the powder was grinded in agate mortar for 45 min with the present of a suitable amount of 2-propanol. It was oven-dried for 1 h at temperature of 60°C, after which the powder was pressed into pellets as explained above and sintered at a temperature of 850°C

### Sample testing

The Tc of the superconducting sample has been measured by

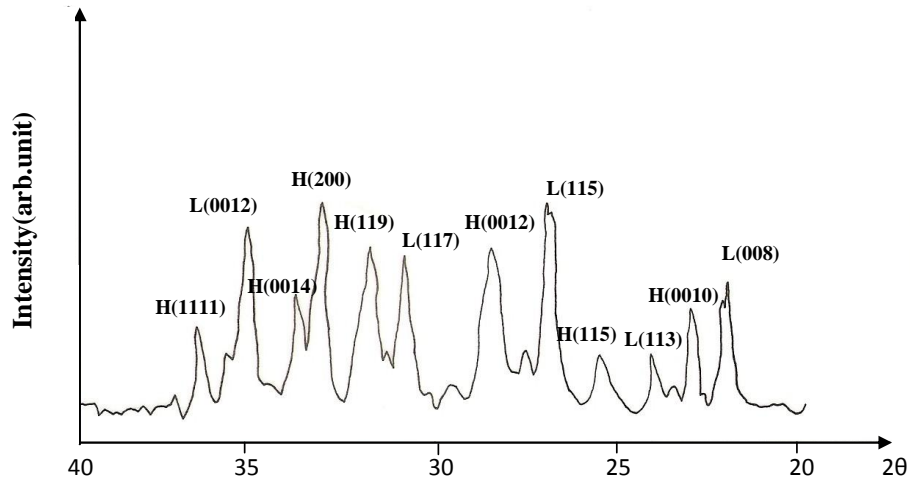


Figure 1. XRD patterns for  $n=3+Pb$  for components  $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4\delta}$ .

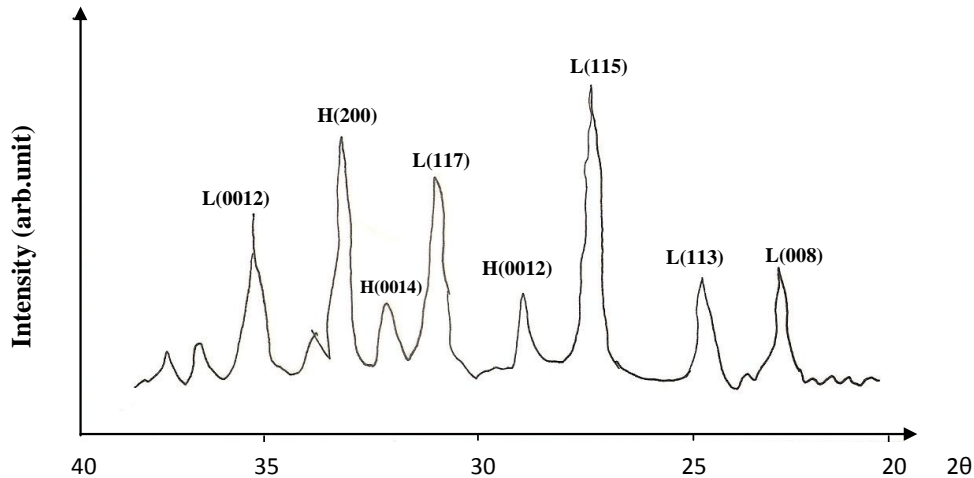


Figure 2. XRD patterns for  $n=3$  for components  $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4\delta}$ .

using the resistivity measurement carried out by four-probe technique, which is considered as a good method for studying the electrical behavior of superconducting materials and a good tool for determining the  $T_c$ , although the last sample was measured roughly by Meissner effect. In this method, a small current is passed through a sample and the voltage drop across it. The terminals distinct from those used for passing the main part of the current through the specimen and the electrical contacts of the sample were made of fine copper wires and adhered with silver paste. The cryostat system was used for the measurement of critical resistivity of the sample, with the presence of liquid nitrogen. The cryostat was joined to a rotary pump to get a pressure of  $\sim 10^{-2}$  mbar inside the cryostat.

#### Structure and surface morphology

The structure of the samples was studied by X-ray diffraction (XRD) type PHELIPS. A computational program has been used to find the

lattice parameter of the unit cell from the pattern of XRD. Fine powder were obtained by grinding the pieces of the samples, then adhered to glass substrate and examined by the X-ray diffract meter. Scanning electron microscope (SEM) type JEOL JSM 6400, was used to study the surface morphology and grain size of the samples for the composition  $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$  with different values of  $n$  and  $Pb$  addition.

## RESULTS AND DISCUSSION

XRD patterns of  $Pb$  doped  $Bi_2Sr_2Ca_2Cu_3O_{10}$  and undoped high temperature superconducting cuprate (HTSC). These are presented in Figures 1 and 2, respectively. Figures 3 to 5 present the XRD patterns of  $Pb$  doped  $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4\delta}$  for  $n=3.5$ ,  $n=4$  and  $n=4.5$ , respectively.

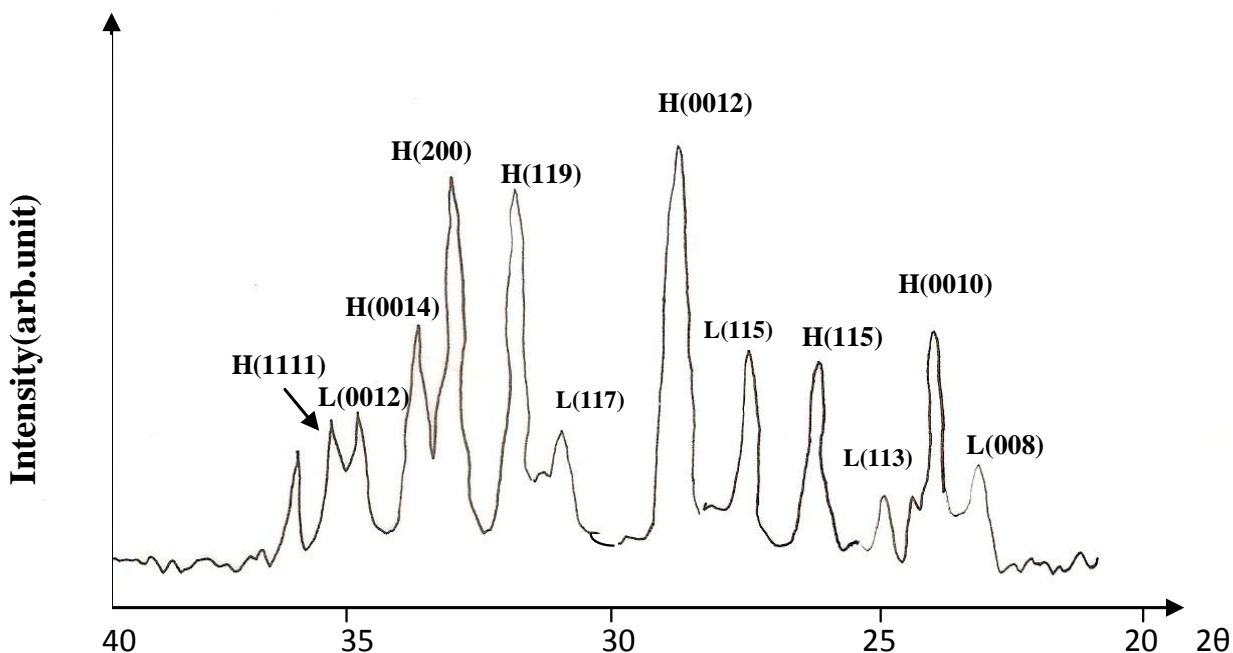


Figure 3. XRD patterns for  $n=3.5 + \text{Pb}$  for components  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$ .

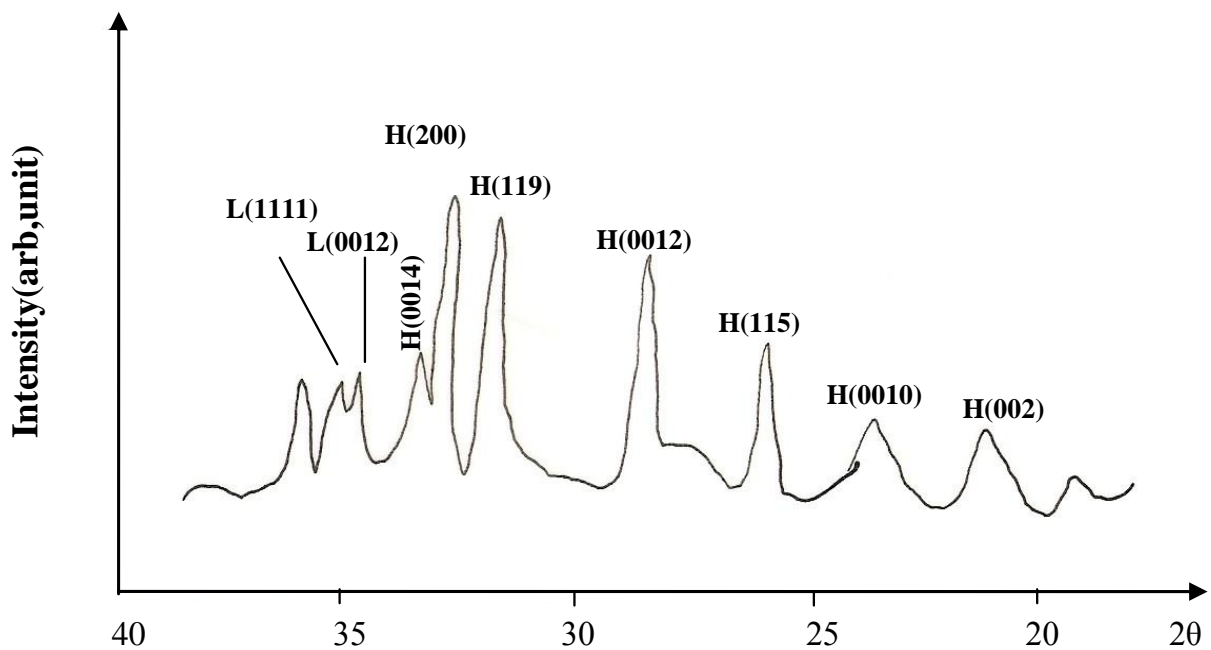


Figure 4. XRD patterns for  $n=4 + \text{Pb}$  for components  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$ .

The lattice constants are calculated as [( $a=5.4102\text{\AA}$ ,  $b=5.4069\text{\AA}$ ,  $c=37.978\text{\AA}$ ); ( $a=5.4079\text{\AA}$ ,  $b=5.4109\text{\AA}$ ,  $c=37.1893\text{\AA}$ ); ( $a=5.4094\text{\AA}$ ,  $b=5.411\text{\AA}$ ,  $c=37.1447\text{\AA}$ ) and ( $a=5.4126\text{\AA}$ ,  $b=5.4142\text{\AA}$ ,  $c=37.1747\text{\AA}$ )] for ( $n=3$ ,  $n=3.5$ ,  $n=4$  and  $n=4.5$ ) Pb doped systems.

The presence of Pb in the structure of Bi-2223 compound has a direct influence on the increase of the high- $T_c$  phase, which can be seen clearly in the XRD pattern in Figures 1 and 2. In the first one, the high- $T_c$  phase reflection (0010, 115 and 1111) is created and the

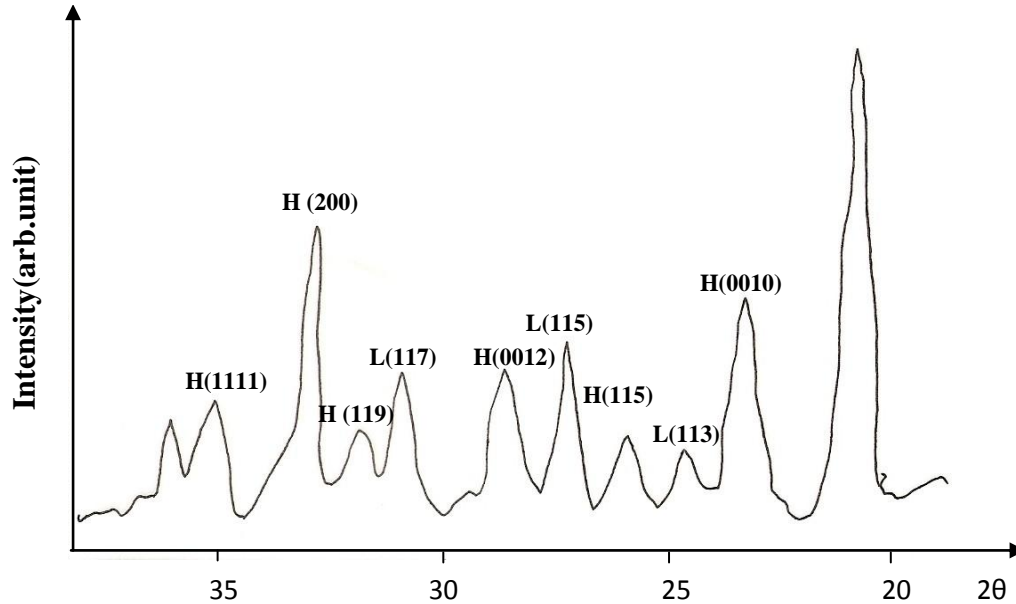


Figure 5. XRD patterns for  $n=4.5 + \text{Pb}$  for components  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+46}$ .

intensities of the reflection (0012, 119 and 0014) are increased by the addition of Pb. At the same time low-Tc phase reflection (008,113,115,117 and 0012) were reduced compared to the same reflections in Figure 2. We conclude that  $\text{Pb}^{2+}$  ions occur in a parallel plane between the Bi-O and Sr-O sheets on the c-axis at distance of 3.7, 3.09 and  $2.065\text{\AA}$ . The  $\text{Pb}^{2+}$  ions may occupy the Bi-positions (Vasumathi et al., 1990) or the Ca positions (Oota et al., 1988) and the presence of Pb in Bi positions enhances the structure stability of the superconducting phases (Mizuno et al., 2010; Cloots et al., 1993). Our experiments also revealed that the addition of Pb lowers the optimum sintering temperature required to form the high-Tc phase to about 848 to  $850^\circ\text{C}$ . This could be attributed to the presence of the  $\text{CaPbO}_4$  phase in the system (Chavira et al., 1988), which changes the kinetic process of the formation of the Bi-2223 high-Tc phase.  $\text{CaPbO}_4$  melts at  $822^\circ\text{C}$  and thus induces a liquid phase below  $850^\circ\text{C}$  and increases drastically, through a dissolution process, the diffusion of the reactive species ( $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$ ). The Pb thus acts as a flux allowing the formation of the 2223 phase in a temperature range in which the Bi-2223 phase is thermodynamically stable (Mizuno et al., 2010; Cloots et al., 1993). The volume fraction of high-Tc phase present in the samples was measured using the following relation:

$$\text{Volume fraction of high-Tc phase \%} = \frac{I_H(0012)}{[I_H(0012) + I_L(115)]} \times 100$$

A computer program was used as a helpful tool for the determination of the cell parameters. The XRD patterns

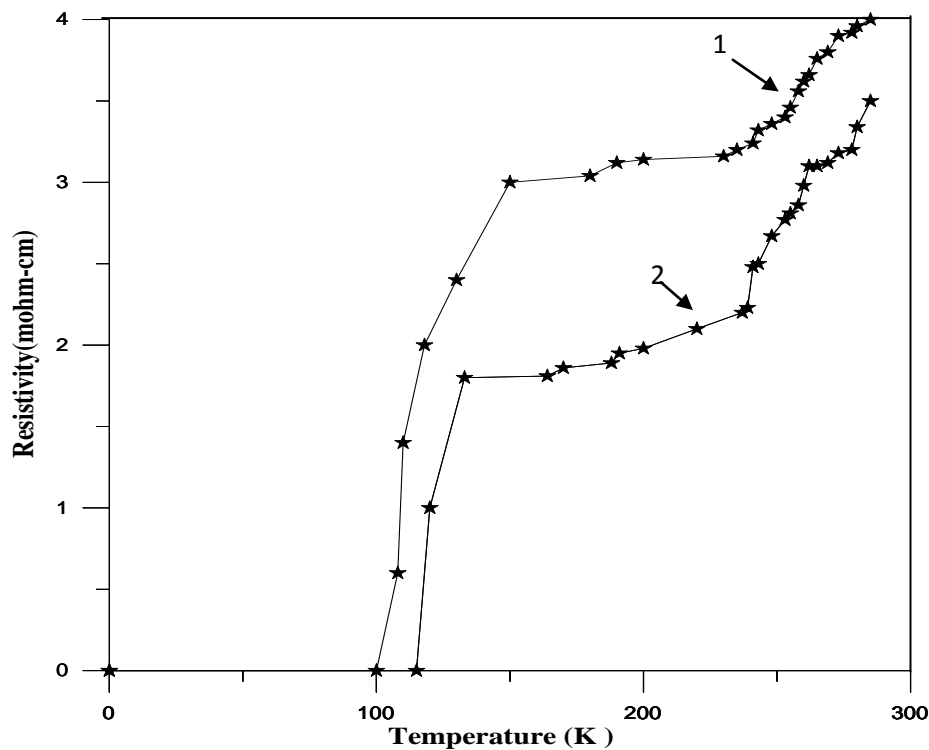
for different values of  $n$  are shown in Figures 1 to 5. It can be noticed that the samples are mixture of a major high-Tc phase and a minor low-Tc phase; the intensity of the high-Tc phase reflections is greater and the peaks are sharper than those of the low-Tc phase.

Mizuno et al. (2010) reported that effective methods to increase the volume fraction of high-Tc phase for Pb-Bi-Sr-Ca-Cu-O system are starting from nominal compositions with more Ca and Cu than in Bi-2223 and the addition of Pb to Bi-Sr-Ca-Cu-O system, and annealing at  $870^\circ\text{C}$  under higher oxygen pressure than 0.2 atm. Chavira et al. (1988) confirmed that the volume fraction of high-Tc phase is rapidly increased, when a small amount of Pb are incorporated in the Bi-Sr-Ca-Cu-O system. They showed that the XRD patterns reveal the possibility for Pb to occupy Ca or Bi sites and in agreement with our results.

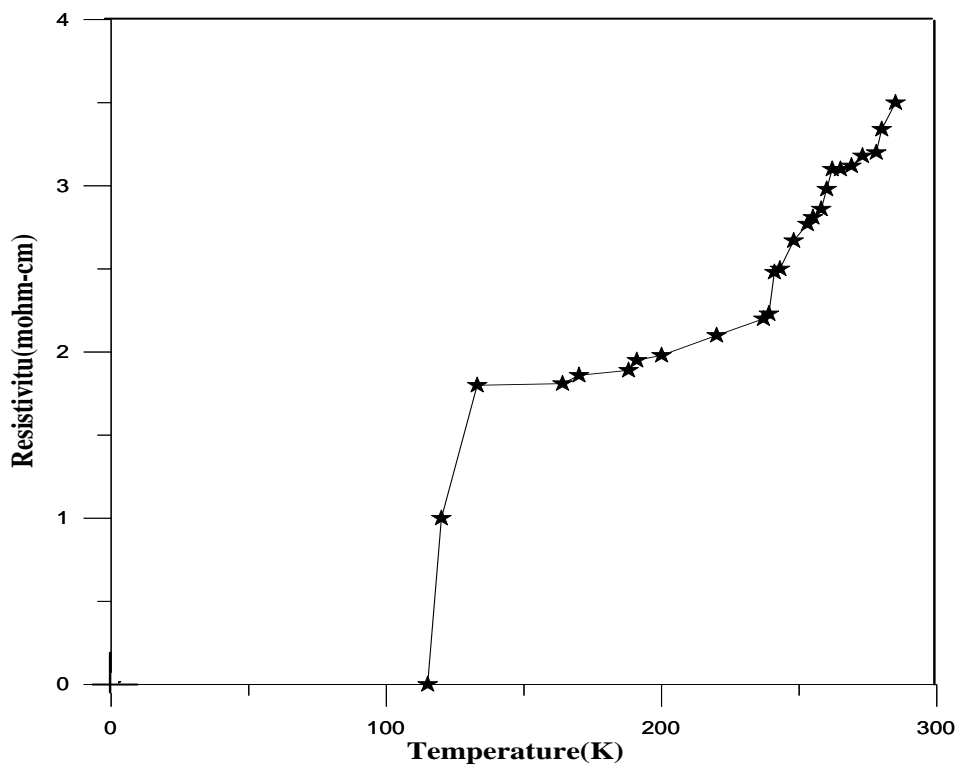
The resistivity of the sample was measured as a function of temperature using standard four-probe technique. For the prepared  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  sample, the onset  $T_c$  is at 108K and the resistivity drops to zero at 100K.

Figure 6 shows the resistivity measurements versus temperature and values of  $T_c = 108\text{K}$  and  $T_c = 133\text{K}$  for the undoped and Pb-doped HTSC samples, respectively. Figures 7 to 10 show values of  $T_c = 133\text{K}$ , 115K, 145K and 127K for samples ( $n=3$ ,  $n=3.5$ ,  $n=4$  and  $n=4.5$ ) Pb doped systems, respectively.

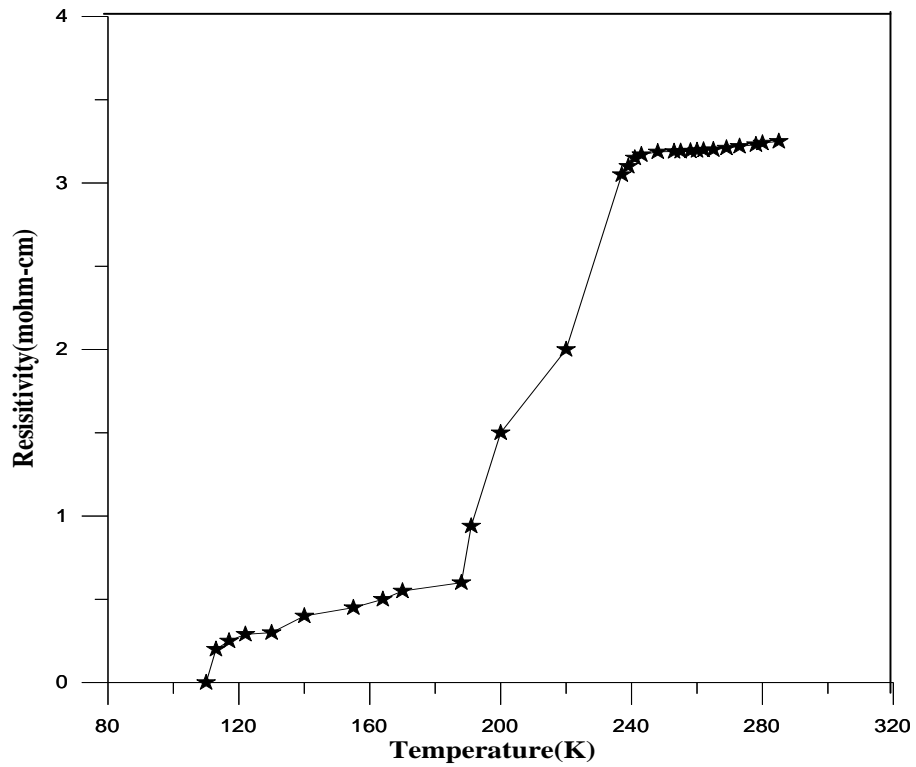
The SEM observing the surface fractures for all samples ( figures 11-14) show the plate-like morphology which is characterized by thin elongated grains with the tendency to align parallel to each other. For  $n=3$ , the grains are elongated platelets and their size are between



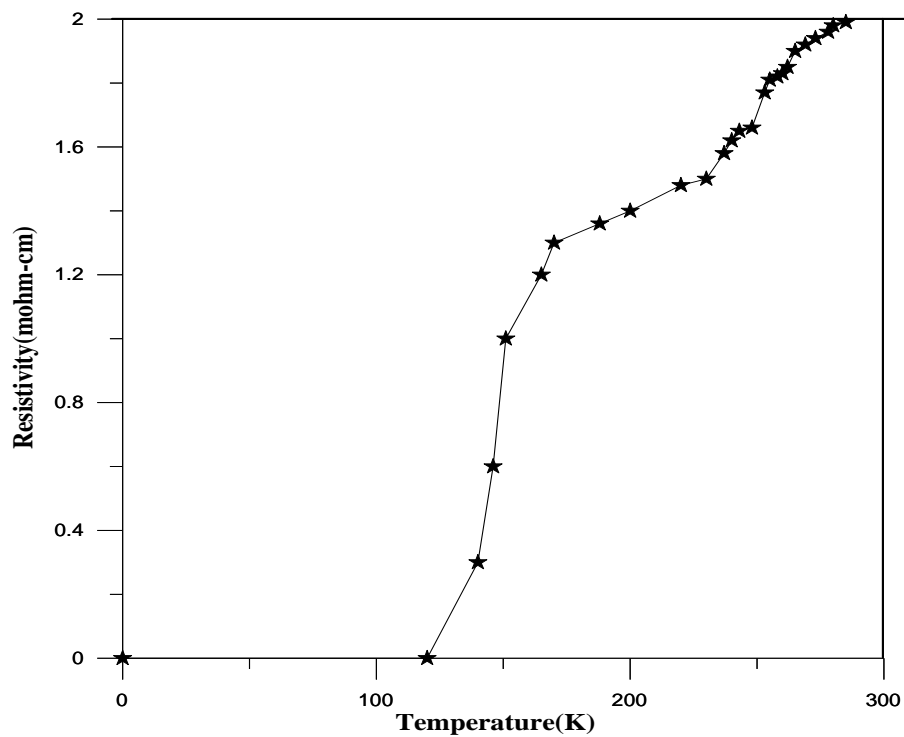
**Figure 6.** The resistivity versus temperature for HTSC (1) without Pb  $T_c=108K$ ; (2) With Pb  $T_c=133K$ .



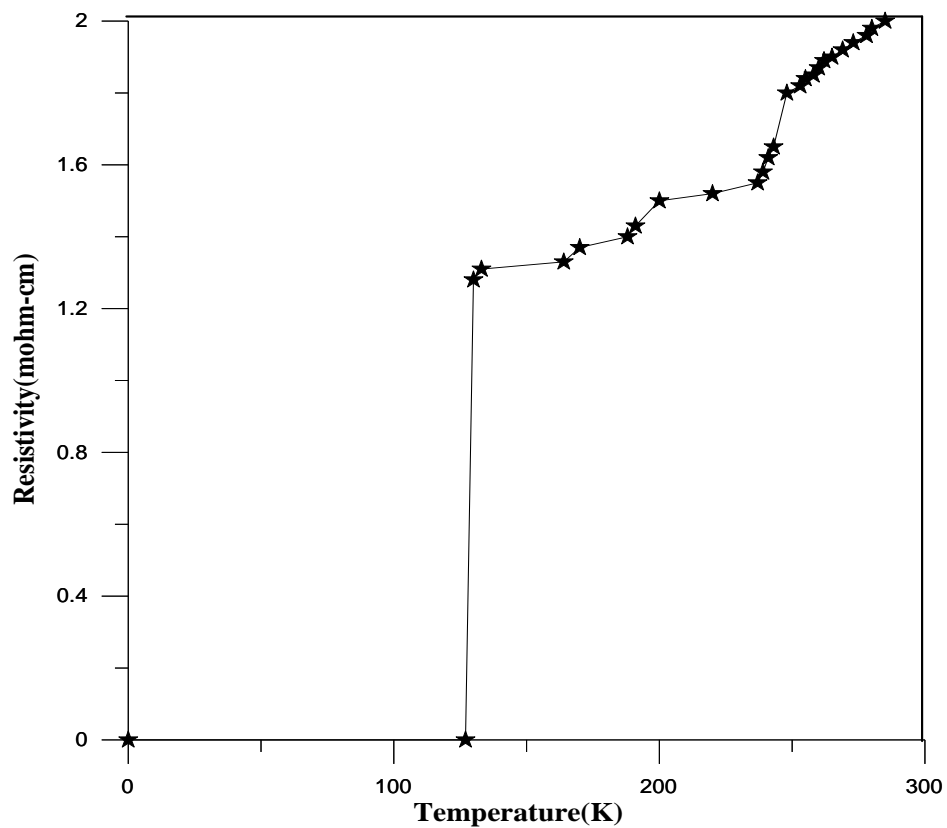
**Figure 7.** The resistivity versus temperature for HTSC  $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4\delta}$   $T_c$ , 133K;  $n$ , 3+Pb.



**Figure 8.** The resistivity versus temperature for HTSC  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta} + \text{Pb}$ .  $T_c$ , 115K;  $n$ , 3.5+Pb.



**Figure 9.** The resistivity versus temperature for HTSC  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta} + \text{Pb}$ .  $T_c$ , 147K;  $n$ , 4.



**Figure 10.** The resistivity versus temperature for HTSC  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta} + \text{Pb}$ .  $T_c$ , 127K;  $n$ , 4.5 + Pb.

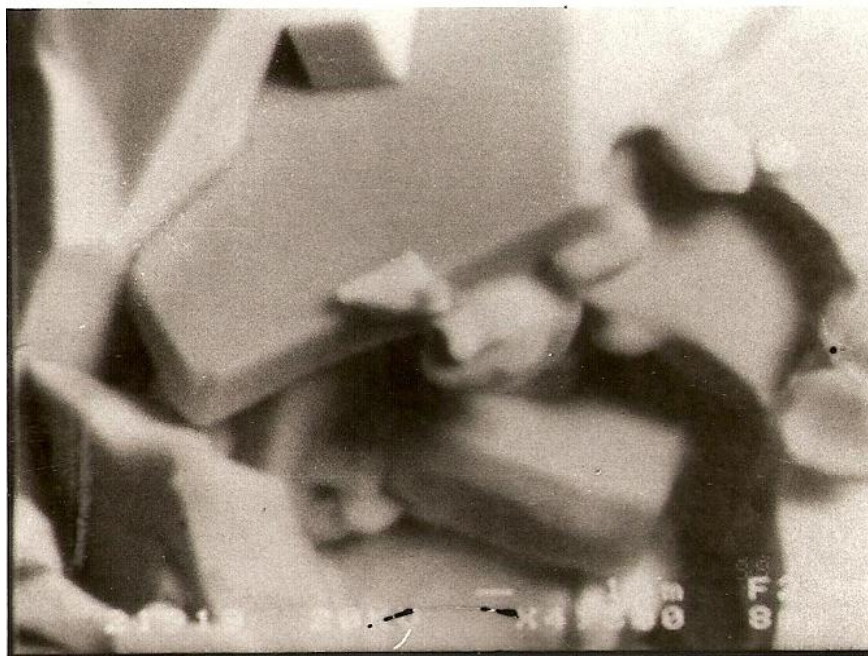


**Figure 11.** Morphology of fracture surface of compound  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$ .  $n$ , 3 + Pb.





**Figure 12.** Morphology of fracture surface of compound  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$ ,  $n$ , 3.5 + Pb.



**Figure 13.** Morphology of fracture surface of compound  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$ ,  $n$ , 4 + Pb.

5 to 9  $\mu\text{m}$  in addition to these particles; they are small grains of 1 to 1.9  $\mu\text{m}$ . According to Primo et al. (1992) these aggregates of small grains are mixture of the  $\text{Ca}_2\text{CuO}_2$  and  $\text{CuO}$ .

When  $n=3.5$  and  $n=4$ , the size of the plate's shape become large than those when  $n=3+\text{Pb}$  the size of grains become as large as 48  $\mu\text{m}$  or even larger. The composition with  $3.5 \leq n \leq 4$  seems suitable to grow grains



**Figure 14.** Morphology of fracture surface of compound  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+46}$ ,  $n, 4.5 + \text{Pb}$ .

of high- $T_c$  phase. Many of these are needle like and big ones are bundle like and these may be responsible for the highest  $T_c$  that has been achieved in this study. The grains of samples  $n=4.5$  have the same size. Syono et al. (1988) showed that the XRD patterns and SEM images of  $\text{Bi}_3\text{Sr}_3\text{Ca}_2\text{Cu}_4\text{O}_y$  compound reveals a structure derived from the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  type in which double bismuth layers along the  $c$ -axis and the orthorhombic unit cell dimensions showed an approximate relation of  $a=\sqrt{2}ap$ ,  $b=\sqrt{2}ap$  and  $c=8ap$ , where  $ap=3.82\text{\AA}$  the parameter of a cubic perovskite and their appearance are similar to samples of  $n=3$  presented earlier.

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